Effect of annealing on Cu precipitates in H ion irradiated Fe–0.6%Cu studied by positron annihilation

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Abstract

Fe–0.6%Cu alloy was irradiated with H ions to 0.1 dpa, and then annealed for 30 min from 150 ^{o}C to 500 ^{o}C. We focused the evolution of Cu precipitates in irradiated Fe–0.6%Cu alloy after the isochronal annealing from the perspective of positron annihilation. The ΔW parameters after thermal annealing (400 ^{o}C and 500 ^{o}C) were much larger than that induced by 0.1 dpa H irradiation. Annealing could promote the aggregation of the Cu-vacancy complexes, and form the Cu cluster–vacancies complexes. When the vacancy-like defects recovered around 500 ^{o}C, it meant the formation and growing of the defect-free Cu precipitates.

Keywords: Cu precipitate; H ion irradiation; Positron annihilation; FeCu alloy

1. Introduction

In our previous report [1], we studied the correlation between Cu precipitates and irradiation defects in Fe-Cu alloys. The Cu precipitate was origin from the formation of the Cu-vacancy complexes, and the coarsening depended on the growth of vacancy-like defects. In Zhang et al.[2], we recently published a paper of our results concerning the effect of annealing on V_mH_n complexes in H ion irradiated Fe–0.3%Cu alloy. We mainly described the interaction between H and vacancy-like defects. However, the ultrafine Cu precipitate is an origin of the irradiation-induced embrittlement, which is considered as one of the menaces to the reactor safety [3]. It has long been known that the small bcc Cu precipitates are initially coherent with the bcc Fe matrix [4, 5]. The size and composition of the small Cu precipitates in both model alloys and steels were extensively examined using atom probe [6-9], small angle neutron scattering [6, 10, 11] and transmission electron microscopy (TEM) [4, 6, 12, 13]. In the present paper, we report a powerful method to examine the evolution of small Cu precipitate which uses the positron as a probe. As well known, positron is not only a sensitive probe for vacancy-like defects. What's more, it could be trapped by nanosize embedded particles (for instance, the Cu precipitates of ~1 nm) in materials [3, 5]. Cu precipitates are easily formed in Fe-Cu alloy during thermal aging and high-energy particle irradiation. Ion beams are very efficient tools for the simulation of the radiations produced in nuclear reactors. Heavy-ion damage took the form of dislocation loops in pure Fe and A533B

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steel irradiated with the dose of ~1 dpa at ~300 ºC [14, 15]. A large number of tiny dislocation loops appeared in pure Fe irradiated with ~1.42 dpa D ion at room temperature [16]. However, once the D ion irradiation fluence decreases to 1×10^{19} D_2^+/m^2 (~0.1 dpa) at room temperature, no obvious dislocation loop formed in the Fe-9Cr alloys [17]. In our previous experiment, the Ni-base alloy C-276 was irradiated by ~120 keV argon ions at room temperature. Compared to the unirradiated sample, there was no obvious change at 0.28 dpa in TEM results. Until to the 0.8 dpa, many tiny black spots appeared in the specimen [18]. For the Cu precipitate in Fe-Cu alloy, there should be important differences between irradiation microstructural development at room temperature and at elevated temperatures. At elevated irradiation temperature of 300 ºC, Xu et al. established that ultrafine Cu precipitates are nucleated before the formation of vacancy clusters [19], and such conclusions are probably not applicable to room temperature irradiations. In the present paper, we discuss the difference for Cu precipitates between induced by low dose H ion irradiation at room temperature and by thermal aging from the perspective of positron annihilation. The evolution of Cu precipitates in irradiated Fe–0.6%Cu alloy after the isochronal annealing is investigated by the Doppler broadening (DB) spectra based on a slow positron beam.

2. Experimental details

The model alloy, Fe–0.6%Cu alloy, was also melted from Fe (99.99% purity) and Cu (99.999% purity) in vacuum using a high-frequency induction furnace. The experimental methods and the preparation of the specimen were the same with the previous report [2].

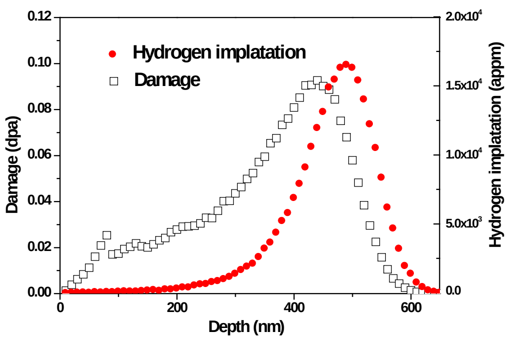

Fig. 1. SRIM calculated damage and deposition profiles for H ion irradiated Fe–0.6%Cu alloy.

The specimen was irradiated with 100 keV H ions to a dose of 0.1 dpa at room temperature, and the current density was ~2μA/cm^2. The damage distribution and H atom deposition profiles calculated by SRIM-2008 are shown in Fig. 1, where the displacement energy was 40 eV. The damage rate is about 5.5×10^{-5} dpa/s. The 0.1 dpa irradiated specimen was annealed isochronally for 30 min in a vacuum of 10^{-5}Pa, and the annealing temperatures were at 150 ºC, 200 ºC, 300 ºC, 400 ºC and 500 ºC, respectively. Positron annihilation DB spectra were performed to characterize the evolution of small Cu precipitates and the vacancy-like defects. S represents the smaller Doppler shift resulting from the annihilation of valence electrons. Thus, compared to a

well-annealed sample, the increase in S for the post-irradiated one comes from the annihilation at vacancy-like defects. W comes from the annihilation with Cu 3d electrons, which is used to estimate the density of Cu atoms around positrons when they are annihilated. The presents of vacancy-like defects and Cu precipitates are represented by the relative S and W parameter, i.e., ($\Delta S = S_n - S_{\text{not irradiated}}$) and ($\Delta W = W_n - W_{\text{not irradiatede}}$), respectively.

3. Results and discussion

The dependence of the ΔS parameter on positron energy for Fe–0.6%Cu alloy irradiated at 0.1 dpa indicates that no expected peak formed in Fig. 2a, which is due to the vacancies were occupied by H atoms. A larger number of H atoms deposited at the damage area, and the V_mH_n complexes were considered to dominate the microstructure in Fe–0.6%Cu alloy after 0.1 dpa irradiation. D atoms were trapped by vacancies, which could decrease the S parameter in Cu ion irradiated W alloy [20]. Similarly, Troev et al. indicated that the lifetime of vacancies decreased after trapping H atoms [21]. Thus, the formation of the V_mH_n complexes would affect the annihilation of positrons with the electrons at vacancy defects.

A predicted evident ΔS peak appeared in the damage region after annealing treatment. Annealing could desorb the H atoms, and residual vacancy defects would increase the ΔS parameter. Compared to the 0.1 dpa specimen, the ΔS parameter increased after annealing at 150 °C, and it continued increasing at 200 °C (see Fig. 2a). However, the decrease of ΔS means that a small quantity of vacancy-like defects began to recovery at 300 °C. Ono et al. reported that most of D atoms were released at ~200 °C from an D ion irradiated Fe–9Cr–2W ferritic alloy [22]. Thus, most of the H atom can easily escape from vacancy-like defects at ~200 °C, but most of the vacancy-like defects still stay in the alloys. The evolution of the vacancy-like defect is not influenced by H atoms at above 200 °C. The H atom desorption indicates that the vacancies and the vacancy clusters were considered to dominate the microstructure after annealing at 200 °C. The rapidly shrinkage of vacancy clusters by dissociating their vacancies at 400 °C facilitated the ΔS decrease (see the magenta line in Fig. 2a). The ΔS parameters continued decreasing during the annealing temperature from 400 °C to 500 °C. Ishizaki et al. pointed out that the thermal decomposition of the vacancy-like defects in Fe induced by H ion irradiation finished completely between 350 °C and 450 °C [23]. For the positron energy range above ~12 keV, as shown in Fig. 2a (wine curve), the S parameter in the post-irradiated specimen after annealing at 500 °C for 0.5 h recovered nearly to the result before irradiation. This means that mostly of the vacancy-like defects were complete disappearance after annealing at 500 °C.

In addition, the dependence of the ΔS parameter on positron energy in Fig. 2a also shows that the peak in ΔS-E curve appeared and moved closer to the surface as the annealing temperature increases. The vacancy-like defects gradually recovered with the increasing annealing because of the vacancy dissolution from the vacancy-like defects. Some of the vacancies would anneal out due to occupation of interstitial atoms. However, according to the vacancy migration mechanism, partly of vacancies would migrate towards to surface region and the opposite direction.

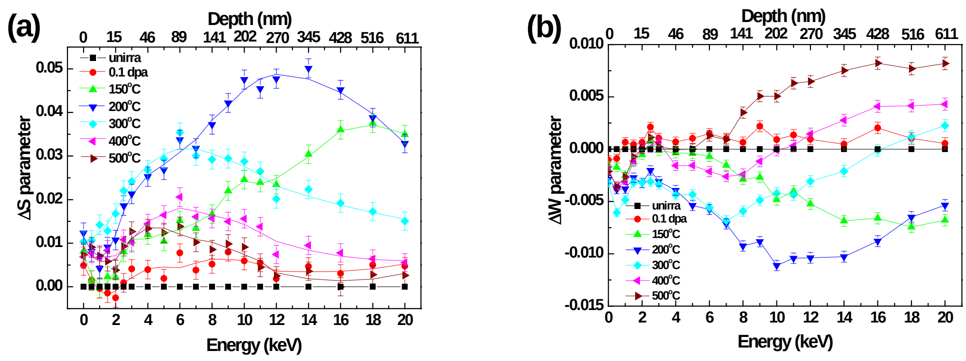

Fig. 2. ΔS-E (a) and ΔW-E curves (b) in 0.1 dpa H ion irradiated Fe–0.6%Cu alloy annealed isochronally, and the annealing temperature were 150 °C, 200 °C, 300 °C, 400 °C and 500 °C, respectively.

Fig. 2b shows the ΔW-E (ΔW parameter-positron energy) curves for Fe–0.6Cu% alloy irradiated at 0.1 dpa and annealed at different temperatures. The positron is a sensitive tool for detecting the Cu precipitates, and it is reported that a coherent precipitate only containing five Cu atoms can trap the positron [3]. Slightly increase of the ΔW parameter was in the 0.1 dpa irradiated specimen (see the Fig. 2b). The increase of the ΔW parameter can be observed only when the positrons are annihilated with the Cu core electrons. As we known that vacancies induced by irradiation are trapped by Cu atoms to form Cu–vacancy complexes when they encountered Cu impurity atoms [19, 24]. The Cu-vacancy complexes would move at room temperature according to the vacancy migration mechanism. Subsequently, they lead to the formation of the vacancy clusters surrounded by ultrafine Cu precipitates (i.e. Cu cluster–vacancies complexes). It is not different from the Cu precipitate formation at elevated irradiation temperature [19]. Once positrons are trapped by vacancy clusters, they are annihilated with the Cu core electrons. The amplitude of the W parameter is proportional to the Cu atom coverage fraction of vacancy-like defects [1]. Thus, the increase of the ΔW parameter in 0.1 dpa irradiated Fe–0.6%Cu suggests the formation of ultrafine Cu precipitates.

After annealing at 150 °C and 200 °C, the ΔW parameters decreased sharply, and then they increased with the increasing of annealing temperature (300°C, 400°C and 500°C). As we discussed above, the annealing can desorb H atoms and recover vacancy-like defects. And, more remarkable, thermal annealing/aging also enhances the Cu precipitates [25]. The changes in S and W are not independent, and S and W values are in an irrigorous inverse relationship in generally. Thus, the ΔW parameters for the annealing at 150 °C, 200 °C and 300 °C were negative due to the observably increase of the ΔS parameters, and the dependence of the ΔW parameter on positron energy was also related to the change of the ΔS-E curves. The Cu precipitate behavior in Fe-Cu alloy thermally aged at below 300 °C, of course, was not obvious. However, with annealing temperature increase to 400 °C and 500 °C, the ΔW parameters were larger than that of only irradiated specimen. It means the Cu precipitate phenomenon has enhanced, which was considered to dominate the microstructure after annealing at 400 °C and 500 °C. First, thermal annealing/aging could facilitate the aggregation of the Cu-vacancy complexes, and increase the Cu precipitate size. Second, the

recovery/dissociation of the vacancy from vacancy clusters at above 400 °C would increase Cu atom coverage fraction of vacancy-like defects. Finally, it leads to the formation and growth of Cu precipitates free from vacancies due to the nearly complete recovery of vacancy-like defects at 500 °C.

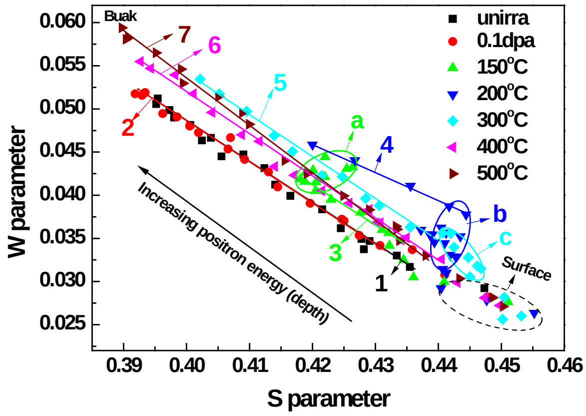

Fig. 3. S versus W plots for the irradiated sample annealed at different temperature, and the (S, W) points of unirradiated sample also included. The gather of (S, W) points are marked by ellipses a, b and c, and they represents the gather region of vacancy-like defects at 150°C, 200 °C and 300 °C, respectively. The surface region of 0~10 nm was also indicated by the dashed ellipse.

S–W correlation represents positron annihilation mechanism after trapped (see Fig. 3). We mainly focused the depth range of 10 nm ~ 611 nm, and neglected the surface region, as indicated by dashed ellipse. Compared to the unirradiated specimen, the slope of 0.1 dpa sample was the same with the unirradiated one (lines 1 and 2). But the range of (S, W) points for 0.1 dpa specimen was slightly increasing along with the increasing positron energy, which further means that the ultrafine Cu precipitates formed by irradiation. With the annealing temperature increasing, all the ranges of (S, W) points for 150 °C, 200 °C and 300 °C annealing (lines 3, 4 and 5) became narrower compared to the unirradiated one. The gather of (S, W) points in the ellipses a, b and c indicated the formation of vacancy clusters, and they were surrounded by ultrafine Cu precipitates. With the increasing of annealing temperature, the gather region of (S, W) points migrated to the surface region, and rapidly shrinkage of vacancy clusters took place at 400 °C. Once the vacancy-like defects has recovered, the ultrafine Cu precipitates would aggregate together. As the annealing increased from 400 °C to 500 °C, the slope and the range of (S, W) points (line 7) increased obviously, which indicated that Cu precipitates coarsened further.

4. Conclusion

Irradiation can lead to the formation of the Cu–vacancy complexes, and their migration and aggregation come to the vacancy clusters surrounded by ultrafine Cu precipitates. The recovery/annihilation of the vacancy dissolution from vacancy clusters at above 400 °C would enhance the Cu atom coverage fraction of vacancy-like

defects, which increased the W parameters. The annealing at 500 ^{o}C would induce to formation and growing of the defect-free Cu precipitates.

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